



Effects of concentration-dependent elastic modulus on the diffusion of lithium ions and diffusion induced stress in layered battery electrodes

Y.-L. He ^{a,b}, H.J. Hu ^{a,b,*}, Y.-C. Song ^{b,c}, Z.-S. Guo ^{a,b}, C. Liu ^{a,b}, J.-Q. Zhang ^{b,c}

^a Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China

^b Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai 200072, China

^c Department of Mechanics, Shanghai University, Shanghai 200444, China



HIGHLIGHTS

- Modulus stiffening enhances the Li-ion diffusion & increases the stress in anode.
- Modulus softening hinders the Li-ion diffusion & decreases the stress in anode.
- The mechanism for effect of varying modulus on diffusion & stress is elucidated.
- Analytic solution of the peak stress considering concentration dependent modulus is given.
- The conditions of neglecting modulus variation during lithiation are obtained.

ARTICLE INFO

Article history:

Received 21 May 2013

Received in revised form

22 September 2013

Accepted 27 September 2013

Available online 7 October 2013

Keywords:

Concentration-dependent elastic modulus

Lithium ion diffusion

Diffusion induced stress

Multilayer electrode

Active layer

Current collector

ABSTRACT

A stress assisted diffusion model considering concentration-dependent elastic modulus of active material has been established for the multi-layered electrodes of lithium batteries. The physical mechanism for the effect of modulus variation on the Li-ion diffusion and corresponding biaxial stress is well elucidated. Moreover, the analytic solutions of maximum stress in both active layer and collector are respectively derived. It has been found that the modulus stiffening gives rise to the additional stress gradient and enhances Li-ion diffusion, therefore to increase the biaxial stress in the plate electrode. In contrast, modulus softening makes the stress assisted diffusion less significant and the corresponding stresses are reduced. These coupled effects are more significant during potentiostatic charging and galvanostatic charging with high charging rates. Moreover, the maximum stress in the active layer is independent of charging process, but depends upon the elastic modulus variation due to Li-ion insertion. Finally, with increasing thickness ratio between collector and active material, the impacts of concentration dependent modulus on the Li-ion diffusion in active layer decreases, whereas this effect on maximum stress in the current collector increases.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Diffusion of lithium ions in electrode is one of the most important processes in the charging and discharging of Li-ion batteries. Stress induced by the diffusion may lead to mechanical degradation such as fracture or fragmentation of the electrode material, and therefore limit the durability and performance of batteries. It is important to describe the Li-ion diffusion and diffusion induced stresses (DISs) accurately.

Diffusion of lithium ions is very complicated because it is affected by many factors, such as concentration gradient [1–4], saturation effects [5], and even the stress induced by the diffusion itself [6–8]. Among the factors stress was found to play important roles. For example, Zhang et al. found that stress gradient significantly enhanced Li-ion diffusion in electrode particles [6]. Gao and Zhou further indicated that stress gradient played much more significant role in the Li-ion diffusions than other factors seen in cathode lattice [7]. Song et al. proposed that the in-plane stress in a bilayer electrode could either facilitate Li-ion diffusion or retard the diffusion depending on the electrode curvatures and bending stresses [8].

The above conclusions are drawn under the assumption that the elastic modulus of active material does not vary during lithiation.

* Corresponding author. Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China. Tel./fax: +86 21 56338345.

E-mail address: huhongj@shu.edu.cn (H.J. Hu).

However, it has been reported that the elastic modulus of graphite tripled in lithiation with the final product of LiC_6 [9], and the modulus of Si decreased from 170 GPa of crystalline Si to 35.4 GPa of $\text{Li}_{22}\text{Si}_5$ [10–13]. Taking such a considerable variation of elastic modulus into account, it is wondered how the stress and stress assisted Li-ion diffusion would be impacted.

Until recently, very few publications have addressed this problem. Deshpande et al. [14] investigated the effect of concentration-dependent elastic modulus on the DISs in a cylindrical electrode particle and reported that moderate modulus softening by lithiation can reduce the fracture tendency at the center of the electrode. However, it was assumed that the Li-ion diffusion is unaffected by stress, and the influence of varying modulus on Li-ion diffusion were not identified. Yang et al. [13] took into account the concentration-dependent elastic modulus for a Cu–Si bilayer electrode and concluded the concentration-dependent modulus is important for stress field but not so important for the Li-ion diffusion process. However, it is still not clear that the mechanism how concentration-dependent modulus impacts the Li-ion diffusion and corresponding DISs.

This work aims to study the impacts of concentration-dependent elastic modulus on the Li-ion diffusion and corresponding DISs in a symmetric layered electrode. An analytic model is established. With the active materials chosen as graphite and Si which are the representative lithiation hardening and softening material, respectively, evolutions of Li-ion concentration and biaxial stresses along plate thickness are examined, with which the physical mechanism for the coupled effect of stress assisted diffusion and concentration-dependent elastic modulus is well elucidated. Moreover, the intensity effect of concentration-dependent elastic modulus was studied systematically under different charging conditions and thickness ratios between current collector and active layer.

2. Methodology

Consider a layered electrode in which two active layers with equal thickness h are symmetrically bonded to a current collector with thickness h_c as shown in Fig. 1. Let the thickness direction be aligned with the z -axis and the in-plane of electrode with x - and y -axes. Li-ions are inserted through the two side surfaces and blocked

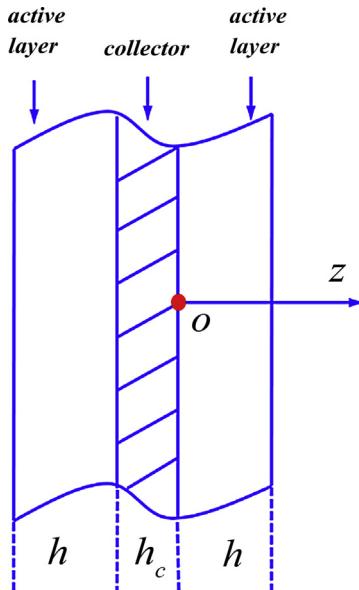


Fig. 1. Configuration of a symmetric multilayer electrode.

by the current collector. The electrode does not bend during charging due to symmetry. Following the analogy between thermal stresses and diffusion induced stresses [5,6,8,13–18], the two non-zero in-plane biaxial stresses in the active layer are given by

$$\sigma_x = \sigma_y = \frac{E}{1-\nu} (\varepsilon_0 - \Omega c/3) \quad (1a)$$

where ε_0 is the in-plane strain, Ω is the partial molar volume of solute, c is the molar Li-ion concentration, E is the biaxial modulus, and ν is the Poisson's ratio.

As Cu is inactive to Li-ion alloying, the in-plane biaxial stresses in current collector can be expressed by simplifying Eq. (1a) as follows,

$$\sigma_x = \sigma_y = \frac{E_c}{1-\nu} \varepsilon_0 \quad (1b)$$

where E_c is the biaxial modulus of current collector.

Here, we focus on a free-standing electrode. The in-plane strain ε_0 can be obtained from the mechanically free boundary condition

$$\int_{-(h+h_c)}^h \sigma_x dz = 0 \quad (2)$$

Substituting Eq. (1) into Eq. (2), we have

$$\varepsilon_0 = \frac{2}{3} \frac{\Omega \int_0^h Ecdz}{E_c h_c + 2 \int_0^h Edz} \quad (3)$$

Substituting Eq. (3) back to Eqs. (1a) and (1b), the biaxial stresses in active layer and current collector can be obtained respectively, when the distribution of Li-ion concentration along layer thickness is determined. It can be found that the stress in the active layer changes with Li-ion concentration, while the stress in the current collector would not vary along the thickness direction as the in-plane strain of the plate electrode is coordinate independent. It is noticed that if the modulus of active layer is constant, the stress in the current collector would be no difference for the Li-ion diffusion, whether it is described by Fick's law or stress assisted diffusion theory. This is because the in-plane strain expressed by Eq. (3) is function of the charge process only if the active layer modulus is invariant. The biaxial stress in the current collector is thus irrelevant with the Li-ion concentration distribution.

In the presence of internal stresses and concentration-dependent elastic modulus, the chemo-mechanical potential takes the following form [13,19]:

$$\mu = \mu_0 + RT\ln c - \Omega\sigma_h - \sigma_h^2 \frac{\partial}{\partial c} \left(\frac{1-\nu}{E} \right) \quad (4)$$

where μ_0 is an invariant reference potential, $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, T is the temperature and $\sigma_h = 2\sigma_x/3$ is the hydrostatic stress. The second term on the right side of Eq. (4) represents the contribution of configurational entropy. Haftbaradaran et al. [5] believed that this term is also impacted by the saturation effect at relatively high Li-ion concentration, and Yang et al. [13] further assumed the saturation affected the Li-ion diffusion flux in the same way. However, more experimental data are required to affirm the mechanism of the saturation effect. Since we focus on the effects of concentration-

dependent elastic modulus, the saturation effect is ignored here. The third term is responsible for the elastic energy induced by Li-ion intercalation under hydrostatic stress σ_h . The last term is a modification to the previous one by considering concentration-dependent modulus.

Li-ion diffusion satisfies the conservation condition

$$\frac{\partial c}{\partial t} = -\nabla \cdot J = -\nabla \cdot (-Mc\nabla\mu) \quad (5)$$

where M is the mobility of Li-ions, J is the ionic flux. Substituting Eq. (4) into Eq. (5), as the diffusion is one-dimensional along z -direction, the diffusion governing equation takes on the following form:

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial z} \left[\frac{\partial c}{\partial z} - \frac{Qc}{RT} \frac{\partial \sigma_h}{\partial z} + \frac{(1-\nu)c}{RT} \frac{\partial}{\partial z} \left(\frac{\sigma_h^2}{E^2} \frac{\partial E}{\partial c} \right) \right] \quad (6)$$

where $D = MRT$ is the diffusivity.

The initial Li-ion concentration is assumed to be zero, i.e.

$$c = 0 \text{ for } t = 0 \quad (7)$$

By symmetry, the right half of the electrode shown in Fig. 1 will be considered here. As Li-ions are blocked by the current collector during charging, the boundary condition at the current collector and active layer interface $z = 0$ is

$$J = -D \frac{\partial c}{\partial z} + \frac{DQ}{RT} c \frac{\partial \sigma_h}{\partial z} - \frac{D(1-\nu)}{RT} c \frac{\partial}{\partial z} \left(\frac{\sigma_h^2}{E^2} \frac{\partial E}{\partial c} \right) = 0 \text{ for } z = 0 \quad (8a)$$

The boundary condition at the inlet surface associated with the charging conditions is

$$J = -D \frac{\partial c}{\partial z} + \frac{DQ}{RT} c \frac{\partial \sigma_h}{\partial z} - \frac{D(1-\nu)}{RT} c \frac{\partial}{\partial z} \left(\frac{\sigma_h^2}{E^2} \frac{\partial E}{\partial c} \right) = i_n/F \text{ for } z = h \quad (8b)$$

for galvanostatic charging, where i_n is the surface current density which is positive for lithiation but negative for delithiation, $F = 96485.3 \text{ C mol}^{-1}$ is the Faraday's constant, and

$$c = c_0 \text{ for } z = h \quad (8c)$$

for potentiostatic charging, where c_0 is the constant surface concentration.

A dimensionless approach is used for above governing equations, initial and boundary condition by $\bar{c} = c/c_s$, $\bar{E} = E/E_0$, $\bar{t} = Dt/h^2$, $\bar{z} = z/h$ and $\bar{\sigma} = \sigma/E_0 Q c_s$, where c_s is the saturation concentration at stoichiometric limit and E_0 is the elastic modulus of pure active layer. Hence, Eq. (6) comes to

$$\frac{\partial \bar{c}}{\partial \bar{t}} = \frac{\partial}{\partial \bar{z}} \left[\frac{\partial \bar{c}}{\partial \bar{z}} - \beta \bar{c} \frac{\partial \bar{\sigma}_x}{\partial \bar{z}} + \frac{2(1-\nu)}{3} \beta \bar{c} \frac{\partial}{\partial \bar{z}} \left(\frac{\bar{\sigma}_x^2}{\bar{E}^2} \frac{\partial \bar{E}}{\partial \bar{c}} \right) \right] \quad (9)$$

where $\beta = 2E_0 Q^2 c_s / 3RT$.

As seen from Eq. (9), the diffusion of Li-ions is driven by the concentration gradient and affected by the biaxial stress gradient and concentration-dependent elastic modulus. The effects of concentration-dependent elastic modulus on the diffusion is characterized by the third item in the square bracket in Eq. (9) and depends on \bar{c} , β , \bar{E} , $\partial \bar{E} / \partial \bar{c}$ and $\bar{\sigma}_x$. Moreover, the magnitude of Li-ion concentration \bar{c} suggests that the concentration-dependent elastic modulus would be more significant at the high concentration place. \bar{E} and $\partial \bar{E} / \partial \bar{c}$ represent the impact of concentration-dependent elastic modulus of active layer. β relies on the properties of active

material and describes how significantly the stress would affect the Li-ion diffusion. However, if the stress related items are removed, the effect of concentration-dependent elastic modulus will completely disappear and the equation degenerates to Fick's law which assumes the diffusion is controlled only by concentration gradient.

The dimensionless boundary conditions of galvanostatic and potentiostatic charging are determined by Eqs. (10a) and (10b), respectively.

$$\begin{aligned} -\frac{\partial \bar{c}}{\partial \bar{z}} + \beta \bar{c} \frac{\partial \bar{\sigma}_x}{\partial \bar{z}} - \beta \frac{2(1-\nu)}{3} \bar{c} \frac{\partial}{\partial \bar{z}} \left(\frac{\bar{\sigma}_x^2}{\bar{E}^2} \frac{\partial \bar{E}}{\partial \bar{c}} \right) &= 0 \quad \text{for } \bar{z} = 0 \\ -\frac{\partial \bar{c}}{\partial \bar{z}} + \beta \bar{c} \frac{\partial \bar{\sigma}_x}{\partial \bar{z}} - \beta \frac{2(1-\nu)}{3} \bar{c} \frac{\partial}{\partial \bar{z}} \left(\frac{\bar{\sigma}_x^2}{\bar{E}^2} \frac{\partial \bar{E}}{\partial \bar{c}} \right) &= \frac{i_n h}{FD c_s} \quad \text{for } \bar{z} = 1 \end{aligned} \quad (10a)$$

$$\bar{c} = c_0/c_s \text{ for } \bar{z} = 1 \quad (10b)$$

Further, the dimensionless biaxial stresses in active layer and current collector can be given, respectively, by the following Eqs. (11a) and (11b):

$$\bar{\sigma}_{a,x} = \frac{1}{3} \frac{\bar{E}}{1-\nu} \left(\frac{2 \int_0^1 \bar{E} \bar{c} d\bar{z}}{(E_c/E_0)(h_c/h) + 2 \int_0^1 \bar{E} d\bar{z}} - \bar{c} \right) \quad (11a)$$

$$\bar{\sigma}_{c,x} = \frac{2}{3} \frac{E_c}{E_0(1-\nu)} \frac{\int_0^1 \bar{E} \bar{c} d\bar{z}}{(E_c/E_0)(h_c/h) + 2 \int_0^1 \bar{E} d\bar{z}} \quad (11b)$$

Hence, it is easy to find that the effect of concentration-dependent elastic modulus on the biaxial stress is related to not only the electrode material properties, but also the structural constraints, i.e. the thickness ratio between the current collector and active layer (h_c/h).

As graphite can be stiffened by Li insertion, whereas silicon can be softened due to Li insertion, the two typical anode active materials are used to investigate the role of concentration-dependent elastic modulus. The active material properties are listed in Table 1. In addition, the active layers are considered as a homogeneous and isotropic continuum medium and its Poisson's ratio is assumed to be independent of concentration. According to the reports on graphite by Qi et al. [9] and silicon by Yang et al. [13], the dependence of elastic modulus on Li-ion concentration can be written as

$$E = 19.25 + 82.234 \times c/c_s \quad (12a)$$

for graphite, and

$$E = 8 + 162/(4.4c/c_s + 1) \quad (12b)$$

for silicon. The variations of elastic modulus by Eq. (12) with the corresponding experimental points against Li-ion concentration

Table 1
Material properties E_0 , Ω , c_s and β of graphite and silicon.

Material	E_0 (GPa)	Ω ($\text{m}^2 \text{ mol}^{-1}$)	c_s (mol m^{-3})	β
Graphite	19.25	4.17×10^{-6} [20]	2.64×10^4 [20]	2.4
Si	170	4.92×10^{-6} [13]	3.65×10^5 [13]	403.9

are illustrated in Fig. 2. The current collector is chosen as copper whose elastic modulus is about 117 GPa.

Based on above derived analytical model, the distributions of Li-ion concentration and the corresponding biaxial stress in a layered electrode can be obtained. However, the stress assisted diffusion with concentration-dependent modulus problem is nonlinear and can only be solved numerically. Therefore, a finite difference method software COMSOL Multiphysics® is used.

3. Results and discussion

The distributions of Li-ion concentration and corresponding biaxial stresses along plate thickness of active layer, as well as the peak stresses in both current collector and active material with and without concentration-dependent elastic modulus during charging are calculated respectively, where the stress assisted diffusions are compared with the diffusion governed by Fick's law which assumes there is no stress coupling.

3.1. Distributions of Li-ion concentration and biaxial stresses along plate thickness

Fig. 3 shows the variations of Li-ion concentration and corresponding biaxial stresses along plate thickness in the symmetric electrode during galvanostatic charging. The charging rate is 1C for all cases. The thickness ratio between current collector and active layer is set as $h_c/h = 0.2$. All the concentrations and stresses are captured at the time corresponding to a SOC (state of charge) of 0.3.

Generally, in all cases the Li-ion concentrations decrease from the side inlet surface into the interior region. The biaxial stresses are compressive in the active layer but tensile in current collector because the lithiation induced expansion of active layer is restricted by the current collector. For both graphite and Si active materials, the stress assisted diffusions facilitate Li-ion diffusion as more ions have been driven into the interior region than those of Fick's diffusion, and it is much more significant in Si electrode with the high coupling factor $\beta = 403.9$, which leads to more uniformly distributed Li-ion concentrations. If the concentration-dependent modulus is accounted, the stress assisted diffusion is further enhanced in graphite which is stiffened upon lithiation but retarded in silicon which is softened in lithiation as shown in Fig. 3(a). The coupled effect of stress assisted diffusion and concentration-dependent modulus may be interpreted as follows.

Considering two particles A and B in the active layer, which subject to hydrostatic stress σ_A and σ_B , respectively (see Fig. 3(b)),

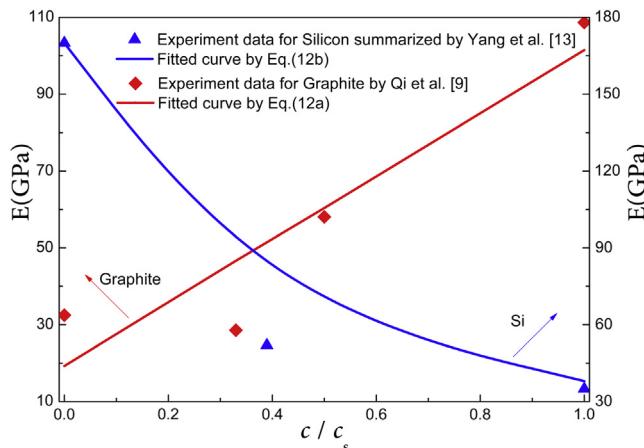


Fig. 2. Concentration-dependent elastic modulus of graphite and silicon.

the change in free energy contributed by stress is $-\Omega\sigma_h$ during lithiation. Being aware that $\sigma_A < \sigma_B$ because the diffusion induced stress in the active layer is compressively higher near the side surface, the stress would do more work if one lithium ion is intercalated into the particle A rather than B. In another word, it is more difficult for lithium ions to be intercalated into a particle with higher compressive stress. Therefore, during lithiation, the compressive biaxial stress facilitates the Li-ion diffusion into the interior region where the intercalation is relatively easier due to lower stresses. For the lithiation stiffening material that $\bar{E} > 1$, i.e. the elastic modulus increases more near the side surface due to higher Li-ion concentration, the stiffening would give rise to additional stress gradient and therefore enhance the stress assisted diffusion. In contrast, for the lithiation softening material that $\bar{E} < 1$, the stress assisted diffusion will be much less significant because the stress gradient is brought down by modulus softening.

The Li-ion concentration near to the inlet surface of the active layer is obvious difference for graphite electrode with and without concentration-dependent modulus, it seems that neglect of the modulus softening leads to very small discrepancy of Li-ion concentration in the Si electrode with the specified thickness ratio between current collector and active layer ($h_c/h = 0.2$), albeit that the elastic modulus of silicon decreases greatly in lithiation. This is consistent with results of Yang et al. [13] who observed that the effects of concentration-dependent Li–Si alloy modulus are significant only on the stress field but negligible on the diffusion process. In order to check this point, it is necessary to further compare the Li-ion concentrations at the inlet surface of Si active material with and without concentration-dependent modulus for different thickness ratio h_c/h and SOC, and the relative discrepancies were calculated by the following Eq. (13) and plotted in Fig. 4.

$$R = \frac{c|_{\partial E/\partial c \neq 0} - c|_{\partial E/\partial c=0}}{c|_{\partial E/\partial c=0}} \text{ for } z/h = 1 \quad (13)$$

As clearly seen in Fig. 4, the relative Li-ion concentration discrepancies R at the inlet surface of Si active layer induced by concentration-dependent modulus depend on the SOC and structural parameters. It sharply increases with decreasing thickness of the current collector relative to active material at the same SOC, and is up to about 40% for the Si electrode with the thickness ratio $h_c/h = 0.1$. Correspondingly, as increase in the SOC, the values of R markedly increase to reach the peak and then gradually drop for each thickness ratio between current collector and active layer. Whatever, it will be underestimated if the modulus softening effect is neglected. Therefore, even for modulus softening electrode, the effect of concentration-dependent elastic modulus may also have a substantial impact on the Li-ion diffusion and should be considered especially for a relatively thinner current collector.

As seen in Fig. 3(b) and (c), the biaxial stress in both the active layer and current collector is remarkably reduced due to stress assisted diffusion, and also obviously affected by concentration-dependent modulus. It would be increased in the graphite electrode where the active material is stiffened due to Li-ion insertion, and decreased in the Si electrode with the lithiation softening active layer. Recently, Deshpande et al. [14] have also found that concentration-dependent modulus has a significant impact on the stress of active material during charging and discharging according to Fick's diffusion equation. However, it can be observed from Fig. 3(b) that the maximum diffusion induced biaxial stress has been greatly overestimated both for graphite (about 121%) and silicon (about 468%) if the stress coupling is neglected.

Fig. 5 illustrates the distributions of Li-ion concentration and corresponding biaxial stresses in potentiostatic charging with the

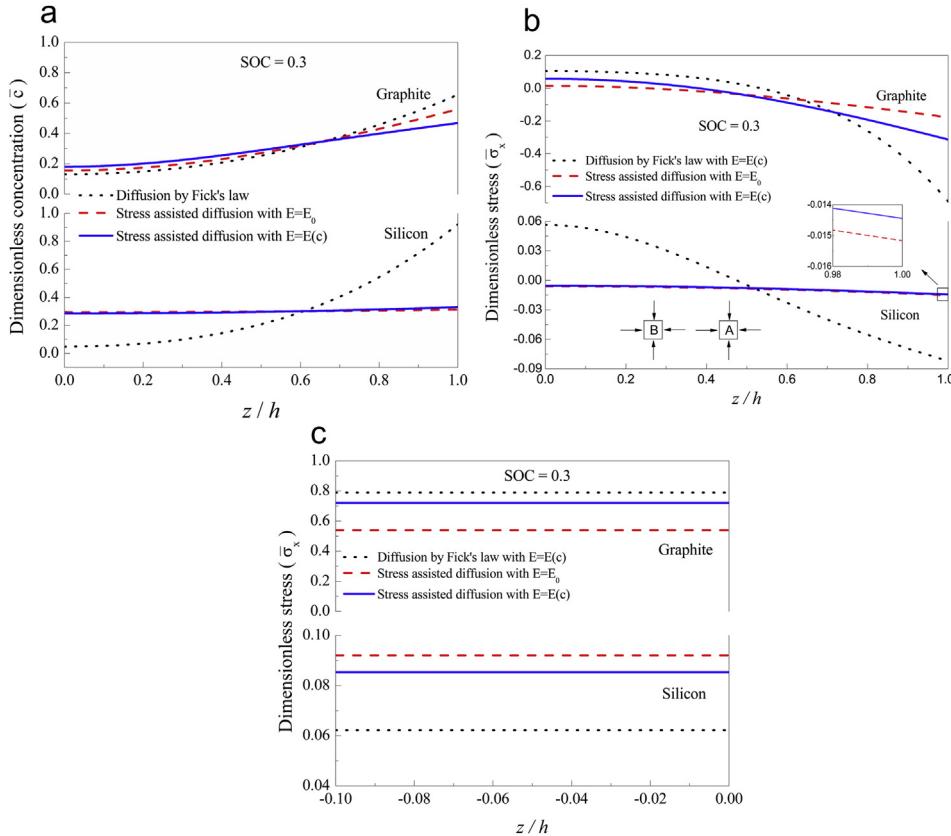


Fig. 3. Distribution of dimensionless Li-ion concentrations (a), biaxial stresses in the active layer (b), and biaxial stresses in the current collector (c) along the plate electrode thickness during galvanostatic charging.

surface concentration $\bar{c} = 1$ at a dimensionless time of $\bar{t} = 0.003$. The stress and concentration-dependent elastic modulus affect the Li-ion diffusion in the similar way as in galvanostatic case, i.e. the stress facilitates Li-ion diffusion and the modulus stiffening/softening makes further impacts by affecting the stress gradient. Different from galvanostatic cases, the ionic flux at the inlet surface is not fixed in potentiostatic charging. Therefore, the stress may increase the intercalation flux at the inlet surface, leading to faster charging and higher Li-ion concentrations as compared with that

by Fick's law. If the concentration-dependent elastic modulus is further considered, modulus stiffening will increase the stress gradient in the graphite electrode, enhance the stress assisted diffusion and lead to even faster charging, whereas modulus softening makes the stress assisted diffusion less significant because the gradient of stress in the Si electrode is reduced.

Similar to that in galvanostatic charging, concentration-dependent elastic modulus has a significant influence on the stress in both the active layer and current collector in potentiostatic charging. However, the impacts of stress assisted diffusion and concentration-dependent elastic modulus on the plate electrode during potentiostatic charging are more significant than galvanostatic charging. This is due to the high Li-ion concentration gradient at the beginning of potentiostatic charging, which leads to high gradients of both stress and elastic modulus and enables significant stress-diffusion coupling. Therefore, it can be concluded that the stress-diffusion coupling and concentration-dependent elastic modulus play more important roles when the Li-ion concentration is high, such as potentiostatic charging and galvanostatic charging with high charging rates.

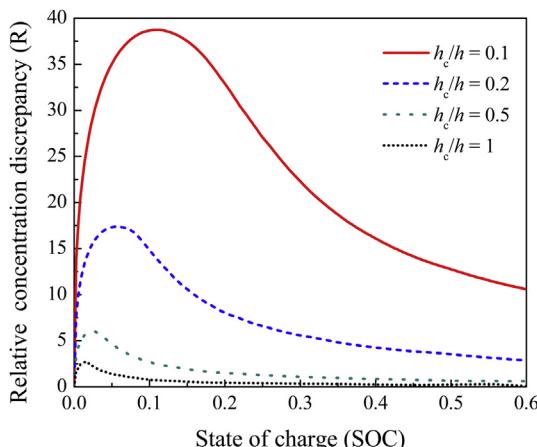


Fig. 4. Dependence of the relative Li-ion concentrations discrepancies at the inlet surface of Si active layer with/without concentration-dependent elastic modulus on the thickness ratio (h_c/h) between current collector and active layer and SOC.

3.2. Evolution of the peak stresses in active layer

As stated above, the peak stresses in the plate electrode are always found at the inlet surface where $\bar{z} = 1$, and combined effects of stress-assisted diffusion and concentration-dependent elastic modulus are more significant in potentiostatic charging. Therefore, only during potentiostatic charging process would the variation of peak stress in the active layer further be studied and plotted in Fig. 6.

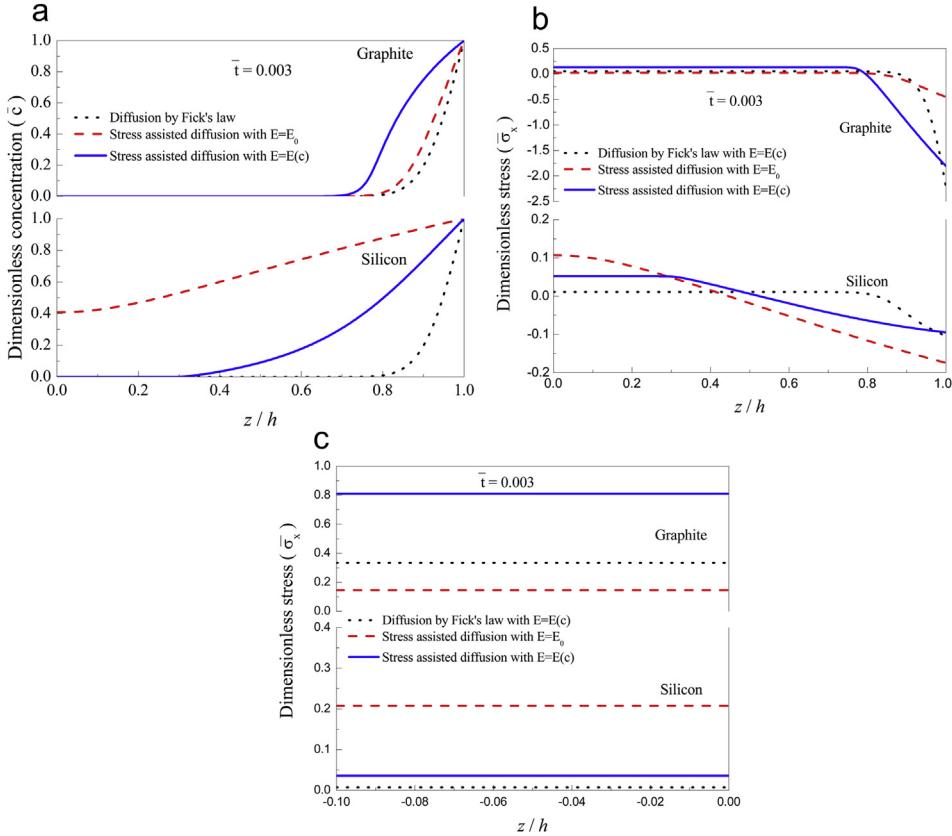


Fig. 5. Distribution of dimensionless Li-ion concentrations (a), biaxial stresses in the active layer (b), and biaxial stresses in the current collector (c) along the plate electrode thickness during potentiostatic charging.

It is found that the concentration-dependent elastic modulus makes significant impact on the peak stress $\bar{\sigma}_a$ in active material where the Li-ion diffusion is controlled by both Fick's law and stress assisted diffusion equation. In graphite electrode the modulus stiffening results in $\bar{\sigma}_a$ being much higher, while in silicon electrode the modulus softening leads to much lower peak stress.

Since the in-plain strain ε_0 is nearly zero and the concentration at the location $\bar{z} = 1$ is $c = c_s$ at the beginning of charging, $\bar{\sigma}_a$ at the inlet surface of active layer would reach the maximum, and can be obtained by simplifying Eq. (11a) as follows.

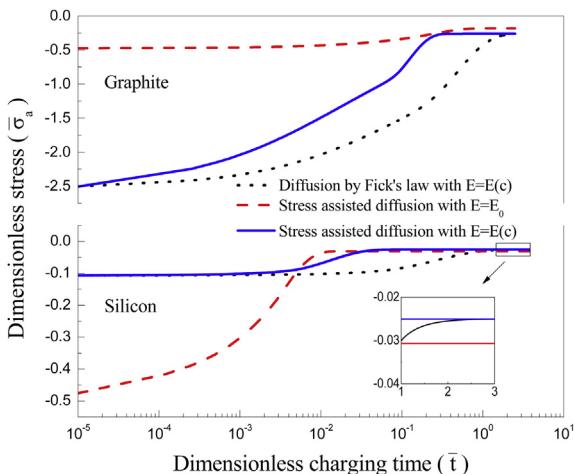


Fig. 6. Evolution of normalized peak stresses in the active layer against dimensionless charging time in potentiostatic charging.

$$\bar{\sigma}_{a,\max} = -\frac{1}{3(1-\nu)} \cdot \frac{E(c_s)}{E_0} \cdot \bar{c}(\bar{z} = 1) = -\frac{1}{3(1-\nu)} \cdot \frac{E(c_s)}{E_0} \quad (14)$$

It is important to notice that $\bar{\sigma}_{a,\max}$ depends upon the Poisson's ratio of the active material and elastic modulus variation due to Li-ion insertion. The relative peak stress difference with and without concentration-dependent elastic modulus, $(E(c_s)/E_0) - 1$ is only related to the elastic modulus variation of the active layer induced by Li-ion insertion. Hence, the maximum of peak stress in the active layer would be decreased at 77.6% for Si electrode, and increased about 427% for graphite electrode due to the effect of concentration-dependent elastic modulus during potentiostatic charging.

3.3. Maximum stress in current collector

According to Eqs. (1b) and (3), the stress in the current collector relies on the concentration-dependent elastic modulus, and it will increase to the maximum when the electrode is charged to full. Further, the dimensionless maximum stress in the current collector can be given as follows.

$$\bar{\sigma}_{c,\max} = \frac{2}{3(1-\nu) \left(\frac{h_c}{h} \cdot \frac{E_0}{E(c_s)} + 2 \frac{E_0}{E_c} \right)} \quad (15)$$

where $\bar{\sigma}_{c,\max}$ is also independent of the charging process, but depends upon the concentration-dependent elastic modulus, material properties and structure parameter of the plate electrode.

As seen in Eq. (15), the values of $\bar{\sigma}_{c,\max}$ increase with decreasing elastic modulus ratio E_0/E_c , and decreasing thickness ratio h_c/h

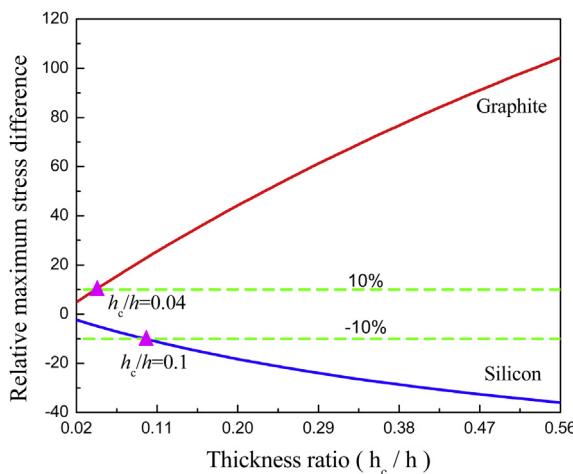


Fig. 7. Relative maximum stress difference $(\bar{\sigma}_{c,\max}(E(c_s)) - \bar{\sigma}_{c,\max}(E_0)) / \bar{\sigma}_{c,\max}(E_0) \times 100\%$ induced by concentration-dependent elastic modulus with respect to thickness ratio between the current collector and active layer.

between the active material and current collector. It is decreased by the softening of elastic modulus upon lithiation that $E_0/E(c_s) > 1$, while increased by the stiffening of elastic modulus upon lithiation that $E_0/E(c_s) < 1$, and the intensity of this variation is mainly dependent on h_c/h . Furthermore, the maximum peak differences induced by concentration-dependent modulus with respect to h_c/h were plotted in Fig. 7.

From Fig. 7, the influence of concentration-dependent elastic modulus on the maximum stress in the current collector would be strengthened with increasing thickness ratio h_c/h . Only $h_c/h \leq 0.04$ for graphite electrode, or $h_c/h \leq 0.1$ for Si electrode, may the effect of concentration-dependent elastic modulus not be taken into account for engineering purpose because the relative differences of maximum stress in the current collector are lower than 10%.

4. Conclusion

An analytical model was developed to study the influences of stress diffusion coupling concentration-dependent elastic modulus on the distribution of Li-ion concentration and biaxial stresses in a symmetric layered electrode of Li-ion batteries. It was found that the internal stresses facilitate the Li-ion diffusion during lithiation, and therefore decrease the stress in both the active material and current collector. The stiffening/softening of elastic modulus upon lithiation further impacted the diffusion by affecting the stress gradient. For a lithiation stiffening material such as graphite, the stiffening would give rise to the stress gradient and further enhance the stress assisted diffusion. For a lithiation softening material such as silicon, the stress assisted diffusion would be less significant because the stress gradient was brought down. Moreover, the effects of concentration-dependent elastic modulus on the Li-ion diffusion sharply increases with decreasing thickness ratio between the current collector and active material, and the relative discrepancies of Li-ion concentration at the inlet surface of active layer with and without concentration-dependent elastic modulus is up to about 40% for the Si electrode ($h_c/h = 0.1$). Correspondingly,

as increase in the SOC, the influences of concentration-dependent elastic modulus on Li-ion diffusion markedly increase to reach the peak and then gradually drop.

Comparing the Li-ion diffusion and diffusion induced stress in the plate electrode during galvanostatic charging with that during potentiostatic charging, it is found that the impacts of stress-diffusion coupling and concentration-dependent elastic modulus are more significant in potentiostatic charging because the gradients of Li-ion concentration and stress are much higher.

The peak stresses in active material are remarkably impacted by concentration-dependent elastic modulus during charge process, and the maximum value can be significantly increased up to 427% in graphite electrode due to stiffening or decreased by about 77.6% in the softened silicon electrode. Finally, the analytical expression of the dimensionless maximum stress $\bar{\sigma}_{c,\max}$ in the current collector was obtained. It was found that $\bar{\sigma}_{c,\max}$ is also strongly affected by the concentration-dependent elastic modulus, and the intensity of this variation would be strengthened with increasing thickness ratio h_c/h between the current collector and active layer. Only $h_c/h \leq 0.04$ for graphite active material, or $h_c/h \leq 0.1$ for Si active material, can the effect of concentration-dependent elastic modulus on the peak stress in current collector be neglected in a layered electrode.

Acknowledgments

The authors gratefully acknowledge the financial supports by the National Science Foundation of China under grant numbers 10672095, 11072137, 11102103 and 11332005, as well as the Shanghai Leading Academic Discipline Project under project number S30106.

References

- [1] M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, *J. Electrochem. Soc.* 143 (1996) 1890–1903.
- [2] R. Deshpande, Y.-T. Cheng, M.W. Verbrugge, *J. Power Sources* 195 (2010) 5081–5088.
- [3] R. Chandrasekaran, A. Magasinski, G. Yushin, T.F. Fuller, *J. Electrochem. Soc.* 157 (2010) A1139–A1151.
- [4] F. Hao, X. Gao, D.-N. Fang, *J. Appl. Phys.* 112 (2012) 103507.
- [5] H. Haftbaradaran, J. Song, W.A. Curtin, H.-J. Gao, *J. Power Sources* 196 (2011) 361–370.
- [6] X.-C. Zhang, W. Shyy, A.M. Sastry, *J. Electrochem. Soc.* 154 (2007) A910–A916.
- [7] Y.F. Gao, M. Zhou, *J. Appl. Phys.* 109 (2011) 014310.
- [8] Y.-C. Song, X.-J. Shao, Z.-S. Guo, J.-Q. Zhang, *J. Phys. D Appl. Phys.* 46 (2013) 105307.
- [9] Y. Qi, H.-B. Guo, L.G. Hector Jr., A. Timmons, *J. Electrochem. Soc.* 157 (2010) A558–A566.
- [10] V.B. Shenoy, P. Johari, Y. Qi, *J. Power Sources* 195 (2010) 6825–6830.
- [11] Z.-W. Cui, F. Gao, Z.-H. Cui, J.-M. Qu, *J. Power Sources* 207 (2012) 150–159.
- [12] J.B. Ratchford, B.E. Schuster, B.A. Crawford, C.A. Lundgren, J.L. Allen, J. Wolfenstine, *J. Power Sources* 196 (2011) 7747–7749.
- [13] B. Yang, Y.-P. He, J. Irsa, C.A. Lundgren, J.B. Ratchford, Y.-P. Zhao, *J. Power Sources* 204 (2012) 168–176.
- [14] R. Deshpande, Y. Qi, Y.-T. Cheng, *J. Electrochem. Soc.* 157 (2010) A967–A971.
- [15] Y. Qi, S.J. Harris, *J. Electrochem. Soc.* 157 (2010) A741–A747.
- [16] T.K. Bhandakkar, H.T. Johnson, *J. Mech. Phys. Solids* 60 (2012) 1103–1121.
- [17] F.-Q. Yang, *J. Power Sources* 196 (2011) 465–469.
- [18] X.-R. Xiao, W. Wu, X.-S. Huang, *J. Power Sources* 195 (2010) 7649–7660.
- [19] F.C. Larché, J.W. Cahn, *Acta Metall.* 33 (1985) 331–357.
- [20] D.-H. Shi, X.-R. Xiao, X.-S. Huang, H. Kia, *J. Power Sources* 196 (2011) 8129–8139.